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PERGAMON

CONCENTRATION OF MERCURY, METHYLMERCURY, CADMIUM, LEAD, ARSENIC, AND SELENIUM IN THE RAIN AND STREAM WATER OF TWO CONTRASTING WATERSHEDS IN WESTERN MARYLAND

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Abstract—Weekly wet deposition and throughfall rain samples were collected in the Blacklick Run (BLK) and Herrington Creek Tributary (HCRT), two streams in western Maryland (MD). Samples were analyzed for total mercury (Hg), methylmercury (MMHg), arsenic (As), selenium (Se), cadmium (Cd), and lead (Pb). Hg concentrations generally fell between 50 and 100 pM, comparable to concentrations in wet deposition measured at other MD sites. While Hg concentrations decreased with rainfall amount, a similar washout trend was not seen for MMHg. Cd, Pb, As, and Se concentrations were comparable overall to those measured in the region. Concentrations of Hg, Cd, and Pb in throughfall were similar between sites and equivalent or higher than wet deposition concentrations. As and Se concentrations were similar in throughfall at the two sites, though throughfall at BLK seemed to be punctuated with slightly higher concentrations of these two metals. Concentrations of Hg, MMHg, Cd, Pb, As, Se, and SPM were measured in monthly stream collections and compared with concentrations found in other MD rivers. In addition to the monthly collections, four storm events were sampled. These measurements demonstrate the importance of storm events in trace metal transport, especially for Hg, Pb and MMHg. For these metals, a strong correlation between metal and suspended particulate concentration was evident. Retention efficiencies of the watersheds for the metals were calculated for each watershed. Of all the metals, Hg is the most and As is the least strongly retained in the watershed. © 2001 Elsevier Science Ltd. All rights reserved

Key words—mercury, methylmercury, rain, stream, trace metals, Western Maryland

INTRODUCTION

Atmospheric deposition provides a large component of the nutrient, especially nitrogen, and trace metal inputs (e. g. Pb, Zn, Cd, As, Se, and Hg), from both natural and anthropogenic (point and non-point) sources, to the Chesapeake Bay (Tyler, 1988; Baker and Clark, 1996; Baker *et al.*, 1997; Mason *et al.*, 1997b; Castro and Morgan, 2000). Power plants and other industrial sources are important contributors of the more toxic elements, such as Hg, Cd, Pb, and the metalloids (As, Se) (DOE, 1996; USEPA, 1997a) and while direct deposition to the Bay's surface is important, runoff from the watershed is also substantial. Past studies suggest that the atmosphere contributes between 25 and 80% of the total N loadings to Chesapeake Bay (Fisher and Oppenheimer, 1991; Hinga *et al.*, 1991; Tyler, 1988; Boynton *et al.*, 1995), and for Hg, a recent mass balance

estimation suggests that about 50% of the Hg entering the mainstem Bay is from direct deposition (Mason *et al.*, 1999). Mercury is strongly retained within the watershed with less than 20% of atmospheric input being transported to the Bay. The other metals are more mobile in watersheds, as suggested by recent studies at Bear Branch (Church *et al.*, 1998) and in Chesapeake Bay tributaries (Lawson *et al.*, 2001). Atmospheric deposition is an important source for Pb, As, and Se, and to a lesser extent for Cd (Scudlark and Church, 1997). Given the importance of anthropogenic sources of these metals and metalloids, and the current regulatory interest on Hg, the metals Hg, As, Se, Cd, and Pb were studied in western Maryland in wet deposition, throughfall, and in two streams for the 1997/98 water year.

The primary objectives of the work were to measure stream water concentrations under base flow and storm flow to further investigate the relationships between flow, particulate load, and metal concentration. Our studies in the Chesapeake Bay tributaries (Lawson *et al.*, 2001) and the results

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of others (Hurley *et al.*, 1995, 1996) suggest that while Hg is strongly associated with particles and shows a flow relationship, this may not be so for other metals. Furthermore, collection of the stream data in conjunction with concentrations measured in both wet only and throughfall deposition allowed an assessment of the retention and fate of the metals and metalloids in the streams. Additionally, the impact of stream chemistry on retention or release of these metals and the impact of these metals on stream biota (Mason *et al.*, 2000a) could be ascertained.

METHODS

All sampling devices (rain collection funnels and connectors, the ISCO® tubing and pump tubing) were acid cleaned prior to use and in between deployments. Rain collection and stream sampling bottles were acid cleaned and stored filled with dilute HCl until needed. All bottles used in storm sample collection were pre-cleaned using these same routine acid-washing procedures (Mason *et al.*, 1999).

Deposition collection

Wet deposition samples were collected at Piney Dam, elevation 780 m, which is located in northeastern Garrett County, MD (Fig. 1) where annual average precipitation (1930–1990) is 1.1 m and about 40% of the total annual precipitation occurs as snow (Stone and Matthews, 1974). Samples were collected using an modified automated wet-only MIC-B collector designed to sample simultaneously for major ions, selected trace metals, and Hg (Landis and Keeler, 1997). The collection system consisted of two 14.3 cm diameter funnels of low-density polyethylene (LDPE) each attached to 1-L HDPE bottles, one for major ion and one for trace metal collection. An additional 17.8 cm diameter glass Hg funnel attached to a 1 L FEP Teflon® bottle was used to collect Hg samples. The Hg connection tube contained a glass insert vapor lock (Landis and Keeler, 1997). All sample bottles were located inside the insulated lower unit of the MIC-B which contained a thermostatically controlled ceramic heater to melt snow and sleet that entered the collection funnels.

Precipitation samples were collected on a weekly basis using ultra-clean sampling techniques. Samples were double bagged and transported to Appalachian Laboratory (AL) where they were weighed and processed for subsequent chemical analyses. A 50 ml aliquot of the major ion sample was used to measure pH and conductivity, and the
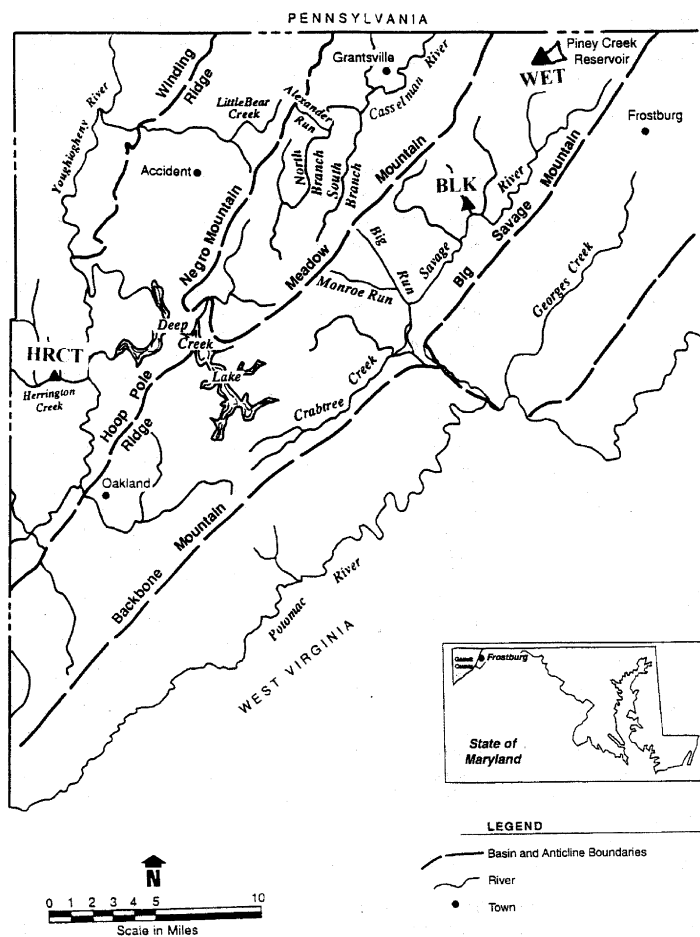
Fig. 1. Map of Western Maryland wet deposition site and stream sampling locations. WET is the wet deposition site at Piney Dam; BLK the site on Blacklick Run and HRCT is the site on the tributary to Herrington Creek.

remainder of the sample was spiked with chloroform and stored at 4°C until analyzed. Samples for trace metal analysis and mercury were frozen until shipment to Chesapeake Biological Laboratory (CBL).

Throughfall samples were collected in two watersheds: (1) the unnamed tributary to Herrington Creek (HCRT), near Oakland, MD; and (2) Blacklick Run (BLK), a stream within the Savage River watershed (Fig. 1). Throughfall samples for trace metals and mercury were collected at three sites in each watershed; one site on each side, approximately 50 m from each stream, and the remaining site in the valley bottom, 10 m from the stream. During the snow-free season, throughfall samples for Hg and metals were collected using 10 cm diameter polycarbonate funnels attached to 1 L FEP Teflon® bottles that were supported by 1 m tall cylindrical PVC tubes (Castro et al., 2000). During the snow season (November–April), throughfall samples were collected in rigorously cleaned HDPE bags (10 mm thickness) supported by 50 cm diameter plastic cans that were attached to 1 m tall permanent posts. Both funnels and bags were deployed simultaneously, side-by-side, at the start of the snow season to compare analyte concentrations in precipitation collected by the two methods. No significant differences in the metal concentrations for the two collection methods were observed.

Throughfall samples were collected weekly. At the time of retrieval of the throughfall samples for trace metals and Hg, large debris (leaf/plant litter, insects, etc.) was removed using plastic forceps and plastic gloves, and the funnels were rinsed with a minimal amount of deionized water in order to facilitate the transfer of residual material adhering to the funnel into the sample bottle. The collection bottle was then detached, capped, doubly sealed in clean plastic bags, and returned to AL for processing. A new funnel/bottle assembly was deployed each week. Trace metal and Hg throughfall samples were frozen at AL and subsequently shipped to CBL for analysis.

Base flow stream collection

Stream water was sampled on a weekly and later monthly basis coinciding with throughfall sample collection. Manual grab samples were collected by filling a 4 L FEP Teflon®-lined HDPE bottle by direct immersion in the stream (after three rinses) upstream from the potentially contaminating sampling equipment (stream height gauge and ISCO® strainer). Samples were obtained under a variety of flow conditions in the stream. Upon retrieval to AL, samples were filtered under a Class 100 clean bench using a peristaltic pump, acid-washed Teflon® tubing and pre-cleaned 0.45 µm pore size filters. The filters were stored in acid-cleaned petri dishes and also frozen. A total sample was taken for each analyte.

Storm events

Storm-flow sampling for trace elements was carried out using an ISCO® Model 3700 automated sequential sampler, which was manually started at the onset of each major runoff event, along with another ISCO® sampler for major ions. The ISCO® sampler was specially modified for trace element sampling as follows: samples were pumped directly from the stream through a polyethylene strainer (to exclude large leaf litter and other debris), which was in turn attached with 9.5 mm I.D. acid-cleaned Teflon® tubing (except for the silicon tubing in the peristaltic pump) to the distributor arm of the ISCO® sampler. Samples were pumped sequentially into 800 mL polypropylene bottles for trace metals after a programmed rinse of the sample lines. Others have also used similar methods to successfully collect trace metal samples using an ISCO® sampler (Church et al., 1998; Bedsworth and Sedlak, 1999; Isaac et al., 1997). For Hg, 350 ml glass bottles were used and the ISCO® sequentially filled a Hg bottle after collection of a trace metal sample. For Hg, samples were decanted from these sample bottles into clean Teflon® bottles as soon as possible after the storm under cleanroom conditions. All ISCO® sample bottles and sampling lines were re-cleaned between deployments. The sampling system was tested by pumping distilled water through the system and comparing concentrations in the feed and processed waters. No contamination was indicated. Additionally, the monthly grab samples were collected within days of the storm samples in February and no discernible difference was found between the concentrations from the ISCO® sampler and the surface grab sample, when normalized for differences in suspended particulate concentration.

Analytical methods

The water samples intended for trace metal analysis were acidified under cleanroom conditions to 1% v/v with Optima® grade nitric acid at least one week prior to analysis to desorb any metal that had been taken up by the plastic bottle but longer holding times had no additional effect. Particulate (filter) samples were digested overnight in a nitric/sulfuric acid mixture at 60°C in Teflon® digestion vessels. Atmospheric deposition (wet-only and throughfall) and stream samples were analyzed for Cd and Pb initially using a Perkin Elmer 3300 Atomic Absorption Spectrophotometer, equipped with a 600 HGA graphite furnace (GFAAS) using standard methods (USEPA, 1997b). After the first month, samples were analyzed using a Hewlett-Packard 4500 Inductively Coupled Plasma Mass Spectrometer (ICP-MS). The metalloids were analyzed by hydride generation-atomic fluorescence techniques, using an automated Merlin PSA analyzer (Lawson et al., 2001).

Standard calibration curves were run daily, and a standard addition spike, added to one in every 15 samples, was used to check for matrix interferences. Externally certified reference samples (digestates of NIST SRM 1646a Sediment for Cd, Pb, As, and Se and IAEA SRM 142 for Hg and MMHg) were also regularly included in the analytical protocols to verify the accuracy of the results. Furthermore, the laboratory participated in the Canadian National Water Research Institute intercalibration in the late summer of 1997 to confirm the analytical methods for trace metals. All results were within the accepted variability. In another study, we compared our sample collection and analysis of river water with those of the Maryland USGS and a commercial analytical company, Frontier Geosciences. All laboratories obtained similar results (unpublished data). Additionally, the laboratory is a regular participant in intercomparisons for Hg and MMHg; the most recent being a comparison of the analysis of Hg and MMHg in Florida Everglades waters organized by Florida DEP for USEPA. Overall, our results compare with those of others (within 20% of the mean for Hg and MMHg, within 10% for the other metals).

Samples were run in duplicate when possible and replicate samples were run on separate days to verify true analytical reproducibility. Field duplicates were collected routinely. Precision was typical for these analyses (Table 1). Samples were analyzed for total Hg and Hg speciation using standard techniques (Bloom and Fitzgerald, 1988; Bloom, 1989; USEPA, 1995). Total Hg was measured in water samples after bromine monochloride (BrCl) oxidation of samples (0.5 mL of 2 N BrCl added; Bloom and Crecelius, 1983) and pre-reduction with hydroxylamine hydrochloride. Samples were then reduced with a tin chloride solution, purged to remove elemental Hg to a gold trap, and the amount of Hg determined by two-stage gold amalgamation cold vapor atomic fluorescence spectroscopy (CVAFS; Bloom and Fitzgerald, 1988). Methylmercury measurements were made, where possible, on precipitation samples (Mason et al., 1997b) and on stream samples by distillation

Table 1. Quality control parameters for the various metals analyses. The detection limit, percentage relative standard deviation for laboratory and field duplicates, typical spike recoveries and field blanks are given for each metal (mercury (Hg), methylmercury (MMHg), cadmium (Cd), lead (Pb), arsenic (As) and selenium (Se))

Metal	DL[a]	% RSD	% recovery of matrix spike	Field blank[a]
Hg	0.5	<20	80–120	<1
MMHg	0.05	<20	80–120	<DL
Cd	0.09	2	95–105	<DL
Pb	0.1	2	90–110	<DL−0.15
As	0.2	<5	90–110	<DL
Se	0.2	<5	90–110	<DL

[a] Detection limit (DL) and blank values are given in nM for all metals except Hg and MMHg which are given in pM.

separation followed by derivitization with sodium tetra-ethylborate, chromatographic separation, and CVAFS (Horvat *et al.*, 1983; Bloom, 1989; Mason *et al.*, 1997a).

For water samples, the detection limits for the various metals and metalloids analyzed are given in Table 1: total Hg 0.5 pM; MMHg 0.05 pM; Cd 0.9 nM; Pb 0.1 nM; As 0.4 nM; and Se 0.4 nM. Detection limits for particulate analyses depended on the sample volume filtered but were generally of the same order as the total metal detection limits. Field and travel blanks were typically less than the detection limit (Table 1).

RESULTS AND DISCUSSION

Wet deposition

Wet deposition concentrations for all constituents from September 1997 until September 1998 are presented in Fig. 2. Concentrations of Hg in rain generally fell between 50 and 100 pM, but there were some events where concentrations exceeded 200 pM (Fig. 2). The volume weighted mean concentration of total Hg was 55 pM for the study period. This mean concentration is similar to that for the 1996/97 sampling period (68 pM) and the range in values (57–75 pM) found at CBL over five years of collection (Mason *et al.*, 2000b). Total Hg fluxes (Table 2) calculated for this study averaged 1.4 nmol m^{-2} week^{-1} and were similar to those measured at Still Pond, Hart-Miller Island, and CBL in 1995/96 (Mason *et al.*, 1997a, b). Generally, high flux values corresponded to lower concentration samples with higher rainfall depth while high concentrations, but low fluxes, were recorded for collections of small volume. This is expected if particulate washout is an important factor contributing to Hg in rain, as shown previously for this site (Mason *et al.*, 1997a). If particulate scavenging is the main process contributing to an element in wet deposition, then the air mass can become depleted of particles during an event, leading to a decrease in concentration in the rain with time, or if the whole rain event is sampled, to a decrease in the overall concentration of the sample. Other studies suggest that while scavenging of particulate Hg is contributing to Hg in rain, other processes are also important (e.g. Mason *et al.*, 2000b). The relationship between rainfall amount and concentration for the current dataset is shown in Fig. 3. Even though the

collections are weekly, the periodicity of storms in the region is such that most weekly samples actually represent only one storm; for example, in 1996/97, which was an unusually wet year (Castro *et al.*, 2000), there were 80 rain days and a number of the storms lasted more than one day. While there is an overall significant ($r^2 = 0.26, p < 0.01$ for $\log Y = mX + c$) exponential decrease in total Hg concentration with increasing rainfall amount, the scatter in the data confirms the notion that other factors are also important (e.g. wind direction). A similar washout trend is not evident with MMHg (Fig. 3), suggesting a minor role for the scavenging of particles in contributing to MMHg in rain. Methyl-mercury concentrations do not seem to indicate any particular seasonal trend either, though concentrations may be slightly elevated in spring/early summer (Fig. 2).

Cadmium and Pb concentrations measured in this study are comparable to those measured in the region in 1994 (Bear Branch Watershed; Church *et al.*, 1998) and to data collected in 1996–1997 at this site (Castro *et al.*, 2000). Cadmium and Pb concentrations appear to track one another between November 1997 and August 1998 (Fig. 2) and their concentrations are linearly correlated ($r^2 = 0.41, p < 0.01$). Concentrations of both Cd and Pb were fairly consistent through all seasons except for Spring (March/April) when they were up to a factor of two higher.

Washout curves (i.e. an obvious decreases in metal concentration with increasing rainfall amount) were evident for Pb and Cd (Fig. 3) if the high spring values are excluded. A washout curve was also visible for Pb in wet deposition collected in Florida (Landing *et al.*, 1995). Clearly, there is some anomaly that accounts for the consistently higher Cd and Pb concentrations during the spring/early summer period as Hg and the metalloids did not show similar elevated concentrations. A logical explanation for these high values cannot be provided at this point, however somewhat higher concentrations for these two metals were found in the streams and throughfall for the same time periods. Overall, the wet deposition fluxes of Cd and Pb were similar to those of the 1996/97 year (Castro *et al.*, 2000) and to those found by Church *et al.* (1998) for the Bear Branch watershed in Maryland.
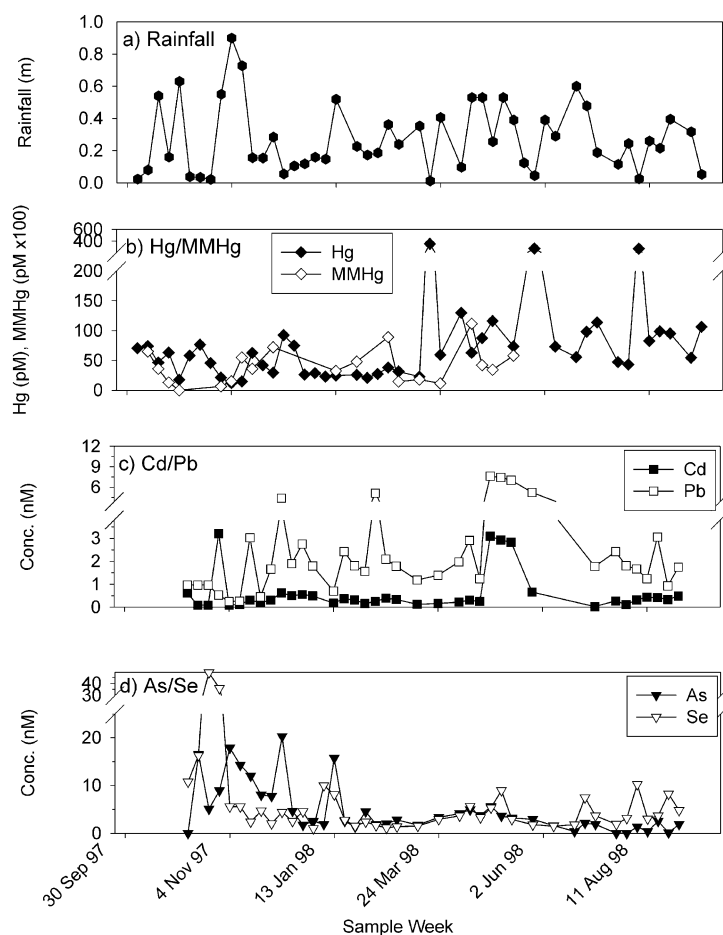
Fig. 2. Rainfall amount per week (m) and concentrations of mercury (Hg), methylmercury (MMHg), cadmium (Cd), lead (Pb), arsenic (As), and selenium (Se) in wet deposition at Piney Dam.

Table 2. Fluxes of mercury (Hg), methylmercury (MMHg), cadmium (Cd), lead (Pb), arsenic (As) and selenium (Se) for wet deposition, and for throughfall collected in the two watersheds—Blacklick Run (BLK) and Herrington Creek tributary (HCRT)

Metal	Wet deposition	BLK-throughfall	HCRT-throughfall
Hg			
Av. weekly flux[a]	1.39 ± 1.18	2.24 ± 3.03	2.29 ± 2.45
Annual total flux[b]	75	129	116
MMHg			
Av. weekly flux	0.016 ± 0.016	—	—
Annual total flux	0.82	—	—
Cd			
Av. weekly flux	0.020 ± 0.042	0.020 ± 0.017	0.024 ± 0.024
Annual total flux	1.1	1.1	1.3
Pb			
Av. weekly flux	0.059 ± 0.080	0.072 ± 0.056	0.11 ± 0.098
Annual total flux	3.1	3.7	5.7
As			
Av. weekly flux	0.051 ± 0.10	0.125 ± 0.16	0.088 ± 0.075
Annual total flux	8.7 (2.6)[c]	6.5	5.1
Se			
Av. weekly flux	0.052 ± 0.11	0.122 ± 0.135	0.087 ± 0.062
Annual total flux	9.0 (3.4)	6.5	5.0

[a] Fluxes are given in $nmol\,m^{-2}$ for Hg and MMHg and in $\mu mol\,m^{-2}$ for Cd, Pb, As, and Se.
[b] The annual flux is calculated by scaling the total measured flux for the weeks where samples were collected to a year.
[c] The values in brackets represent the estimated flux if the high values measured in the early part of the study are ignored (see text for details).
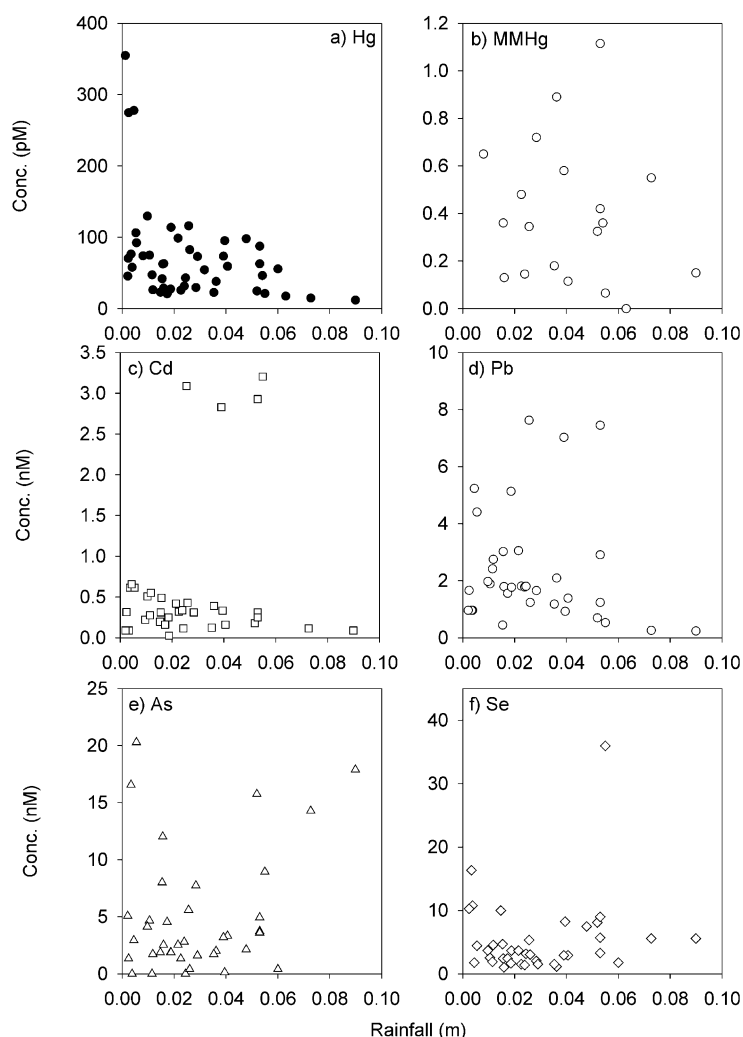
Fig. 3. Concentration of metals versus rainfall amount for wet deposition at Piney Dam.

Arsenic and Se concentrations appear to be higher in Fall wet deposition for the 1997/98 study (Fig. 2) compared to the 1996/97 data, when concentrations of these two elements appeared to be lowest in the Fall (Castro et al., 2000). With the exception of one weekly collection, Se concentrations all fell below 20 nM. There is no obvious reason for these higher concentrations as contamination for these metalloids, but not other metals, is unlikely. There is only minimal evidence of a washout curve for Se (Fig. 3), and no evidence of such a trend for As, suggesting that storm track, and the local input from sources immediately upwind of the site, is more important than rainfall amount in determining concentration and is the dominant control when examining concentrations and fluxes of these metalloids. There are a number of large power plants in close proximity to the Piney Dam site, and these could be important sources of the metalloids (Ondov et al., 1996).

Cadmium, Zn, and As are all released during steel production, while incinerators are also responsible for emitting Cd, Cr, Pb, and Zn (Ondov et al., 1996). Cadmium, As, and Se are bi-products of both local and long-range transport of coal combustion emissions. Metals with similar sources would be expected to track one another if those sources were primarily responsible for the concentrations found in wet deposition. Linear regression analysis of the elements against each other at Piney Dam shows a relatively strong positive correlation between Pb and Cd ($r^2 = 0.41, p < 0.01$ for 1996/97) and between Hg and Pb ($r^2 = 0.12, p = 0.01$). In the (1995/96) study, where samples were collected for Hg and metals on an event basis (Castro et al., 2000), a strong correlation was also seen at this site for Hg and Pb, but not for the other elements, based on a multiple regression of the elements measured (Table 3). In that study, As and Se were strongly correlated with each other and with Pb, but not with Cd. In 1997/98 the correlations were not observed. Clearly, differences in correlations between the two datasets may reflect the fact that event

Table 3. Correlation coefficients between trace metals in rain at three Maryland locations. The Piney Dam data refer to event collections made at the same site to the current study in 1996/97 (Castro *et al.*, 2000). The Science Center site is on the roof of the building in downtown Baltimore. The CBL site is over water on a pier next to the laboratory. Bold numbers are significant at the 95% level

	Cd	Pb	As	Se
Piney Dam 1996/97				
Hg	0.15	**0.49**	0.26	0.28
Cd		0.17	0.41	0.09
Pb			**0.67**	**0.68**
As				**0.56**
Science Center 1997/98				
Hg	**0.49**	**0.56**	**0.70**	**0.64**
Cd		**0.60**	0.38	0.16
Pb			0.40	0.29
As				**0.95**
CBL 1998				
Hg	0.14	0.22	−0.60	−0.82
Cd		**0.95**	0.14	0.01
Pb			0.22	0.04
As				**0.86**

samples were collected in 1996/97 and weekly samples in this study.

For rain collected at the Science Center (SC), an urban site in Baltimore, Hg was strongly correlated with Pb, Cd, As, and Se. This is not surprising given the site's proximity to sources of these metals such as power plants and waste incinerators. Mercury was not positively correlated with any of the other elements for rain collected at CBL, another rural site. However, Pb and Cd were strongly correlated at both SC and CBL (Table 3). In a study conducted in Florida (Landing *et al.*, 1995), As and Pb, but not the other elements, were correlated strongly in wet deposition at rural locations. These results suggest a multitude of Hg sources (coal burning and waste incineration) in the city but a dominance of other sources, perhaps both local and distant, at the more remote locations. The lack of a correlation between Hg and As and Se at the Piney Dam site indicates that other sources besides coal combustion are contributing Hg to precipitation in Frostburg. The positive correlation found between Cd and Pb at most sites suggests incineration as the dominant source of these metals.

The estimated yearly fluxes for the various elements were: 75 nmol m^{-2} for Hg, 8.7 µmol m^{-2} for As, 9.0 µmol m^{-2} for Se, 1.1 µmol m^{-2} for Cd, and 3.1 µmol m^{-2} for Pb (Table 2). The Hg, Pb, and Cd fluxes are within 25% of the values obtained in 1996/97 (Castro *et al.*, 2000). The As and Se values are 3–5 times those found previously. It is possible that these differences could be accounted for, to some degree, by differences in analytical methods. While quantification in both cases relied on hydride generation techniques, much stronger acid digestion was used in this study for the determination of As and Se which may have released additional metalloid from solid matrices, thus accounting for a more complete recovery of these metalloids compared to that of the previous study.

Additionally, however, the magnitude of the fluxes for 1997/98 are dependent to a large degree on four high weekly concentration/fluxes which contribute about 40% of the As flux and 37% of the Se flux, as estimated above (Fig. 2 and Table 2). Eliminating these values, the recalculated fluxes are 2.6 and 3.4 µmol^{-2} yr^{-1}, respectively. There is, however, no clear reason to eliminate these values from the dataset. Given the proximity of Piney Dam to potential anthropogenic sources upwind, the possibility of occasional high precipitation concentrations and deposition due to local impaction of the site by these source plumes is clearly possible.

Other studies have found similar concentrations and fluxes for wet deposition to those reported here. In the Great Lakes area, Hoff *et al.* (1996) found that As concentrations in wet precipitation ranged from 1.3 to 2.6 nM across sites and Se varied between 4 and 9 nM. The average values for this study (vol.wt. mean concentrations of 6.5 and 6.7 nM, respectively) are within a similar range. Sweet *et al.* (1998) report yearly fluxes of 1–1.3 µmol m^{-2} for As and 6.9–8.4 µmol m^{-2} for Se for the Great Lakes area. Gelinas and Schmit (1998) found an average flux of 2.0 µmol m^{-2} for Se for rural locations around Montreal with fluxes up to three times higher for impacted locations. Thus, while the fluxes of As and Se measured at Piney Dam in 1997/98 are higher than those measured in 1996/97, they are comparable to values measured at other impacted locations.

Throughfall

Mercury, Pb, and Cd concentrations (Fig. 4) and depositional flux (Table 2) in throughfall were similar at the two sites. There was no obvious seasonal trend in throughfall Hg concentrations, except for a slight increase in concentration during winter and summer over spring and fall. The concentrations in throughfall for Hg, Pb, and Cd are equivalent or higher than
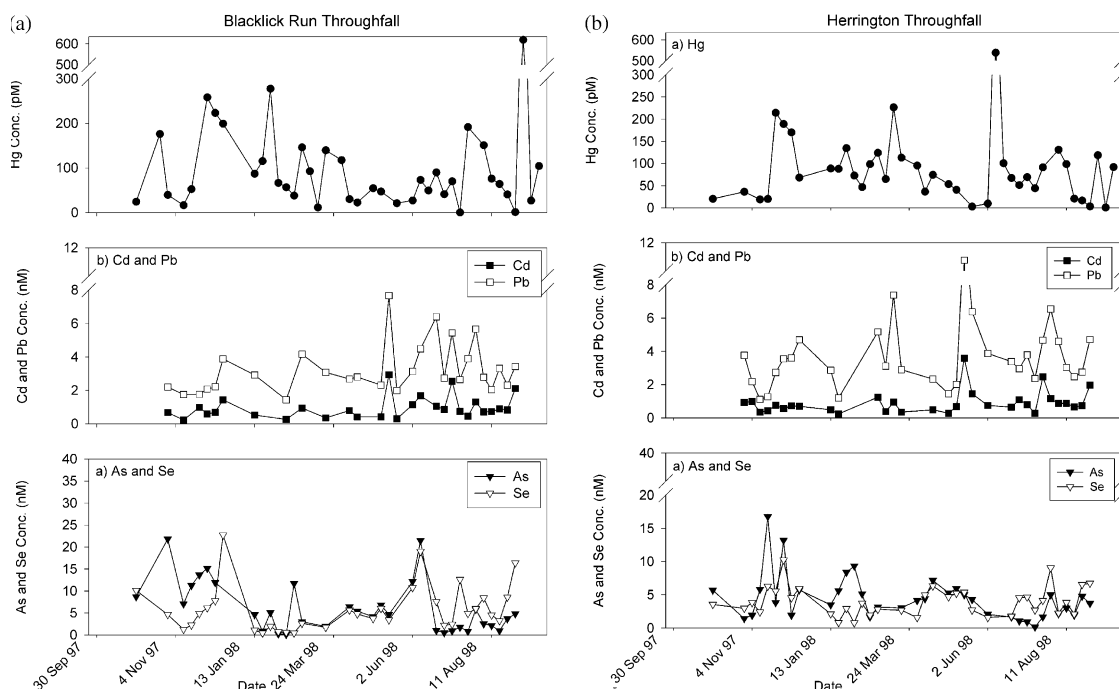
Fig. 4. (a) Concentrations of Hg, Cd, Pb, As, and Se in throughfall at Blacklick Run (BLK) (b) Concentrations of Hg, MMHg, Pb, Cd, As, and Se in throughfall at the Herrington Creek site (HCRT).

that of wet deposition (Table 2). An increased throughfall flux over wet deposition suggests that washoff of dry deposition from leaves is an important component to this flux while a lower throughfall value would suggest uptake of metal by the leaves is occurring. Additionally, local particulate and litter-fall from trees can contribute to this flux. However, in this study, the impact of leaves and large litter was minimized by filtering the sample of large debris upon collection.

The magnitude of the increase in throughfall relative to wet deposition for Hg (a factor of 1.5–2) is similar to that found by others (e.g. Lindberg, 1996). A study by Rea et al. (2000) in upstate Michigan suggested that most of the increase in Hg in throughfall comes from washoff of dry deposited material. This contrasts the results of Guentzel et al. (1998) who suggest that Hg deposited on leaves of trees in Florida is not readily washed off. One reason for the different conclusions of these studies may be the fact that most of the dry deposition of Hg in Florida is as reactive gaseous Hg (Guentzel et al., 1998), while particulate deposition likely dominates in rural Michigan (Rea et al., 2000). The relative increase in throughfall is similar for Pb (a factor of 1.2–1.8) but the highest throughfall flux was in BLK for Hg and in HCRT for Pb. Cadmium showed little enhancement in throughfall flux. This result is consistent with the results of Stachurski and Zimka (2000) who observed Cd adsorption by leaves from rainfall.

For As and Se, the comparison of wet and throughfall is complicated by the lack of throughfall

collection during the initial periods of study when the high As and Se values were measured in precipitation. Taking this into consideration, the As and Se throughfall fluxes are higher than the adjusted wet fluxes for both watersheds, by a factor of 1.5–2. The throughfall flux was somewhat higher for both As and Se in BLK compared to HCRT. Other studies in western Maryland (e.g. the Bear Branch watershed; Church et al., 1998) have found similar relative values for metals in wet compared to throughfall deposition for Cd and Pb. At Bear Branch, wet only fluxes of As and Se were higher than the throughfall fluxes, but this to some degree reflected differences in rainfall amount between sites. Overall, the higher throughfall fluxes indicate net washoff of dry deposited material as the concentration in through-fall likely represents a net process due to uptake of metals from the leaf surface; leaching of metals from leaves during precipitation events; and uptake or leaching from debris in the samples during the period between rainfall and sample retrieval.

Monthly stream samples

The average concentrations of Hg, MMHg, Cd, Pb, As, and Se in the streams for the monthly collections are shown in Table 4. The stream concentrations of all the elements are similar to those found previously in Maryland mountain watersheds (e.g. Castro et al., 2000; Church et al., 1998). Given the low particulate loading ($< 10 \, mg \, L^{-1}$) in these streams under baseflow conditions, the

Table 4. Average total concentrations for the monthly grab samples from each stream for suspended particulate (SPM), mercury (Hg), methylmercury (MMHg), cadmium (Cd), lead (Pb), arsenic (As), and selenium (Se). Concentrations are in nanomolar units except for mercury and methylmercury (picomolar)

Parameter	BLK	HCRT	log K_d BLK	log K_d HCRT
Flow (cm s^{-1})	0.08 ± 0.06	0.04 ± 0.02		
SPM (mg L^{-1})	5.4 ± 11.5	6.4 ± 8.3	—	—
Hg (pM)	8.5 ± 5.3	10.5 ± 4.7	5.57 ± 0.6	5.58 ± 0.5
MMHg (pM)	0.07 ± 0.06	0.30 ± 0.30	6.05 ± 0.3	6.02 ± 0.4
Cd (nM)	0.54 ± 0.80	0.57 ± 0.23	2.92 ± 0.7	2.69 ± 0.5
Pb (nM)	0.26 ± 0.35	1.6 ± 1.7	2.98 ± 0.8	2.69 ± 0.47
As (nM)	0.37 ± 0.21	9.4 ± 6.2	2.85 ± 0.7	2.58 ± 0.4
Se (nM)	0.55 ± 0.45	0.36 ± 0.28	2.83 ± 0.7	2.77 ± 0.6

dissolved phase ($<0.4\,\mu$m) is the dominant fraction under low flow, even for Hg which is most particle reactive of the metals measured. The total Hg concentrations, and the dissolved-particulate distribution coefficients (K_d's), are comparable for both streams. Additionally, the Hg concentrations in these rivers fall within the range of baseflow concentrations (5–15 pM; Lawson *et al.*, 2001) in other rural Maryland rivers (e.g. Susquehanna and Choptank) but fall within a much smaller range than Maryland rivers influenced by urban inputs (e.g. Herring Run and Potomac; 5–20 pM). For MMHg, there are occasions when MMHg concentrations are higher than typical values, as indicated by the large RSD, especially in HCRT (Table 4). Methylation occurs in reduced environments and is likely to have higher seasonal production in summer. It may build up in the wetlands associated with the streams under dry periods, with a resultant release during higher flow and subsequent wetland flushing. The low pH HCRT appears to have a somewhat higher MMHg concentration than BLK. Differences in flow regime, seasonal effects, changing particulate load, as discussed below, and in particulate composition and stream chemistry could all account for the highly variable concentrations over time.

The concentration of Cd was typically low and fairly consistent across the seasons. This results from the fact that Cd is not strongly particle bound (i.e. low K_d; Table 4) in these streams and of all the metals is the least impacted by changes in flow (see below). Cadmium concentrations were slightly higher in HCRT, possibly a reflection of the lower pH of this stream. Carroll *et al.* (1998) concluded that of Zn, Cd, and Pb, Cd was the most mobile of the metals and was strongly influenced by changes in stream pH. Cadmium concentrations in this study were on average about half of those found in many Chesapeake Bay tributaries (<1–2 nM; Lawson *et al.*, 2001).

On average, the concentration of Pb in HCRT and BLK were also lower than those found in other Maryland rivers under baseflow (Lawson *et al.*, 2001). However, Pb levels were high on occasions which corresponded to high Pb concentrations in rain at the same time. Contamination may be the reason for these high concentrations but we consider

this unlikely, as samples from the streams and from deposition were handled by different personnel. In general, As appears to be higher in HCRT while Se appears to be higher in BLK. Arsenic concentrations were highest in the fall of 1997 and tended to decrease throughout the sampling period. Like Pb, the As concentration was higher in the March sampling. The variability between streams could to some degree reflect differences in the input loadings and particulate concentrations at each sampling period.

Storm events

Four storm events were sampled although only two will be discussed in detail. During the first storm on 11/6/97, no particulate measurements were made. The flow increased to 0.65 cm s^{-1} on BLK and was higher on HCRT (1.8 cm s^{-1}). The second event was in early January (1/8/98) and is discussed below (Fig. 5). Two events were sampled in February but the rainfall associated with the first storm on 2/10/98 was concentrated over BLK (maximum flow of 0.31 cm s^{-1} in BLK; 0.04 cm s^{-1} in HCRT). Particulate loads were only slightly elevated—<15 mg/L. An event on 2/17/98 was also sampled (Fig. 6). For all events, there was a good correlation between flow and SPM.

The January event had the highest flow and SPM concentrations at the start of sampling and they decreased exponentially with time. The SPM loads were as high as 34 mg L^{-1} for HCRT (Fig. 5b) and above 100 mg L^{-1} for BLK (Fig. 5a). Total Hg and MMHg concentrations were elevated in BLK and decreased in concert with the decrease in SPM. Total Hg, but not MMHg, was also substantially higher in HCRT during the storm event. Lead was elevated in BLK in the early stages of the storm, while Cd levels in HCRT were consistently elevated throughout the event. A strong difference in Cd concentration between streams is clearly evident during this storm, as it was for the other storms and the monthly grab samples. Interestingly, As was high in both streams in contrast to Se. The decrease in SPM with time was exponential in BLK (Table 5) and most of the metal concentrations showed a similar pattern. The exponential decay relationship
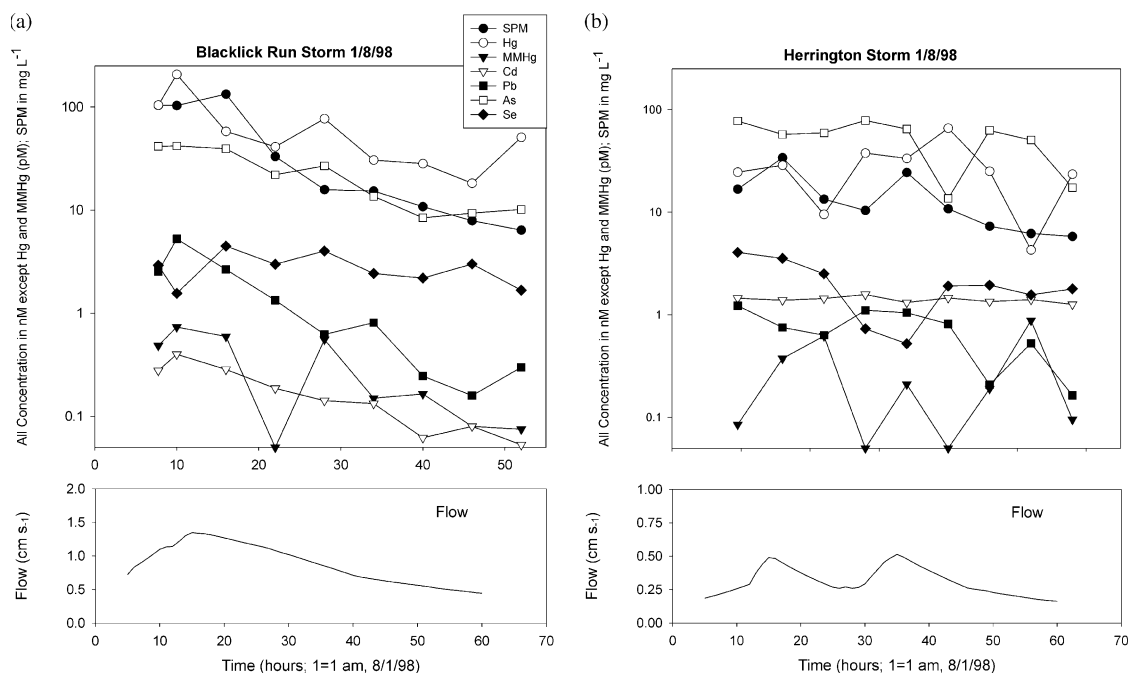
(a) (b)

Fig. 5. (a) Concentrations of suspended particulate matter (SPM), Hg, MMHg, Cd, Pb, As, and Se and the hydrograph during the 1/8/98 storm at BLK. (b) Concentrations of SPM, Hg, MMHg, Pb, Cd, As, and Se and the associated hydrograph during the 1/8/98 storm at HCRT. Note that symbols used are the same for all the data in Figs 5 and 6.

Table 5. Parameters for correlation plots against time for the 1/8/98 storm for Blacklick Run for suspended particulate (SPM), mercury (Hg), methylmercury (MMHg), cadmium (Cd), lead (Pb), arsenic (As), and selenium (Se). The slope (m) of the relationship for $\log Y = mX + c$ is tabulated as well as the correlation coefficient (r^2) and the level of significance (for $n = 9$, $p < 0.01$ for $r^2 > 0.64$; $p < 0.05$ for $r^2 > 0.44$)

Parameter	Slope, m	Corr. Coeff., r^2	p value
SPM	−0.031	0.91	<0.01
Hg	−0.015	0.55	<0.05
MMHg	−0.020	0.48	<0.05
Cd	−0.019	0.93	<0.01
Pb	−0.031	0.87	<0.01
As	−0.017	0.88	<0.01
Se	−0.003	0.06	N.S.[a]

[a] Not significant.

was significant for all elements except Se. Additionally, the slope of the relationships were within a factor of two suggesting that changes in particulate load was the major control over the measured concentrations.

The hydrograph was more complex in HCRT during this storm and the clear patterns in BLK are masked as a result. However, the importance of SPM in driving concentration is not lost, and is especially evident for the more particle-reactive elements such as Hg. Again Se shows no trend with time, and for HCRT, As is less well correlated with flow or SPM.

The storm sampled on 2/17/98 (Fig. 6) showed similar trends. Higher SPM concentrations were recorded on both streams for this event, and Hg and Pb concentrations tended to follow the change in SPM and flow. For the other metals, the response

was less discernable. Se concentrations were similar to previous events but As concentrations were lower overall. Again, the flow response for HCRT (Fig. 6b) was more complicated than that of BLK (Fig. 6a), but Hg still tracked the SPM and flow changes closely. Combining the information from the three storms where SPM was measured, and the baseflow data, the relationship of the metals to SPM can be further demonstrated (Table 6). The relationships were always stronger for BLK than for HCRT and Hg and Pb, and to a lesser extent MMHg, were significantly correlated with SPM ($p < 0.01$) for both streams while Cd and As were significantly correlated with flow for BLK but not for HCRT. In both streams, Se concentrations was little influenced by SPM or flow (Table 6). It is not known why the correlations are stronger for BLK compared to

(a)

Blacklick Run Storm 2/17/98

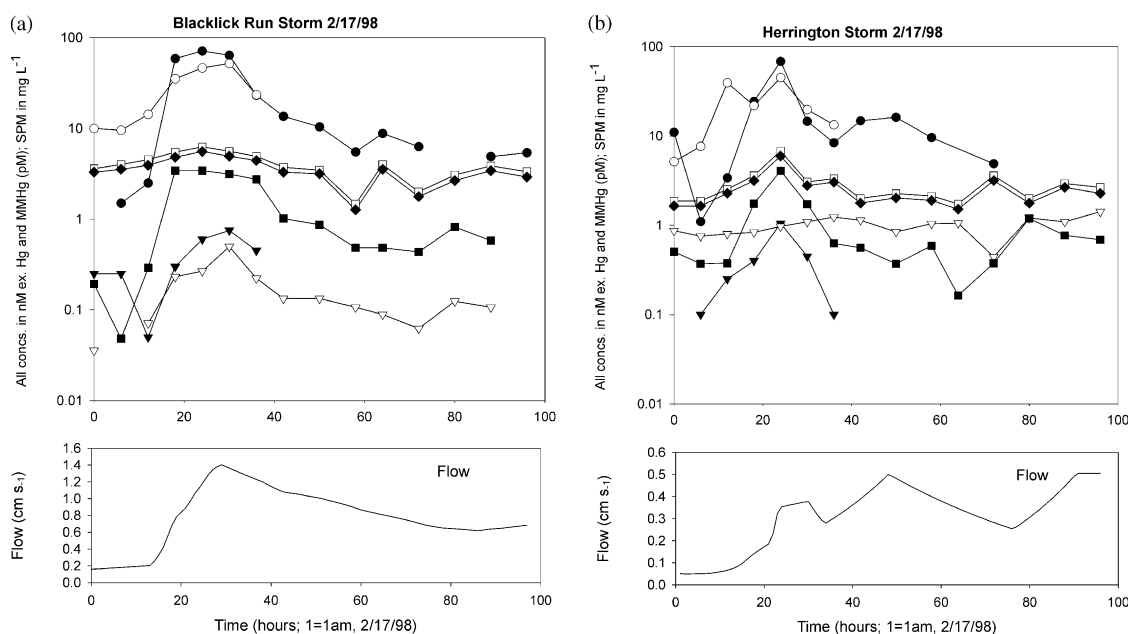(b)

Herrington Storm 2/17/98

Fig. 6. (a) Concentrations of SPM, Hg, MMHg, Cd, Pb, As, and Se and the hydrograph during the 2/17/98 storm at BLK. (b) Concentrations of SPM, Hg, MMHg, Cd, Pb, As, and Se and the hydrograph during the 2/17/98 storm at HCRT. See Fig. 5 for the symbol legend.

Table 6. Correlation parameters (slope and r^2 for $Y = mX + c$) for the relationship of each measured metal/loid—mercury (Hg), methylmercury (MMHg), cadmium (Cd), lead (Pb), arsenic (As), and selenium (Se)—against suspended particulate (SPM). For the dataset ($n = 30-35$, depending on parameter), a r^2 value of > 0.22 is significant at $p < 0.01$; $r^2 > 0.14$ for $p < 0.05$

Parameter	BLK			HCRT		
	Slope	r^2	p value	Slope	r^2	p value
Hg	0.83	0.55	<0.01	0.55	0.27	<0.01
MMHg	0.005	0.56	<0.01	0.009	0.17	<0.05
Cd	0.002	0.24	<0.01	0.015	0.04	N.S.
Pb	0.031	0.74	<0.01	0.032	0.35	<0.01
As	0.25	0.63	<0.01	0.24	0.02	N.S.
Se	0.007	0.03	N.S.	0.05	0.21	<0.05

HCRT but one reason might be the much higher SPM load in this river, and the higher flows generally during the monitored events. The slopes of the significant regression lines are similar (Table 6) suggesting that the concentration of the metals on particles is not significantly different between the two streams.

The overall results suggest that for BLK and HCRT, Hg, Pb and MMHg are strongly associated with particulate matter, especially at the higher loadings. A correlation between Hg, Pb and SPM (or flow) was also found in several other rivers in and around Maryland during both base and storm flow (Lawson *et al.*, 2000). Overall, total Hg concentrations at HCRT were lower than those at BLK during storm events and this correlates with the generally higher SPM values at BLK during storms compared to HCRT. Only in BLK were MMHg concentrations significantly correlated with SPM. Also, when %

MMHg is examined with respect to SPM, a significant relationship is not found, and % MMHg actually appears to decrease with increasing SPM concentration. Similar behavior of % MMHg with respect to SPM was seen in other Maryland rivers (Herring Run, Potomac). Again, as was true for MMHg concentrations in the monthly grab samples, % MMHg was visibly higher in HCRT than in BLK, but on both rivers, % MMHg was generally 5% or less of the total Hg; this is commonly found in other rivers in Maryland (Lawson *et al.*, 2001).

Distribution coefficients (K_d's) for the monthly grab samples further illustrate the strong binding of Hg and MMHg to particulate matter (Table 4). In our studies of both small and large tributaries of the Chesapeake Bay, we have found similar log K_d values for Hg (range, on average, 5.1–5.5). For Pb and Cd, K_d values for these two streams are lower than those found in other Chesapeake Bay tributaries (Pb and

Cd averages ranged from 3.6 to 4.7) and in Wisconsin Rivers (Shafer *et al.*, 1999). In Wisconsin, K_d values varied by more than an order of magnitude, with much of the variance related to differences in organic content of the water and of the particles. The low K_d's found in this study likely reflect the low organic content of the particulate matter in the Western MD streams under baseflow conditions (1–2 mg L^{-1} total organic carbon). There is little information in the literature for the distribution of As and Se between dissolved and particulate phases. Our values suggest that these metalloids are not strongly particle reactive in these streams.

Mass balance budget

To examine input-output budgets, percent retention was estimated for each stream. The yearly stream flux or watershed yield (in mol m^{-2}) was estimated using representative baseflow and high flow concentrations for each metal on each stream, and the available flow data (Table 7). This yield estimation method, which includes both baseflow and storm flow sampling and daily averaged flow data, has been shown to give results comparable (typically within 10%) to a regression approach (Swistock *et al.*, 1997), especially for elements that show a strong concentration-flow relationship. Combining this error with the analytical errors of measurement leads to an estimate of the error in the yield calculations. The overall error is about 40–50% for Hg, 20–30% for the other elements.

Overall, about 40% of the water flow occurs under high flow regimes and thus storm events dominate the flux for the more particle-reactive elements. The Hg yields are similar for the two streams and are comparable to that of other rural Maryland watersheds (Lawson *et al.*, 2000). The yield of MMHg from HCRT is about twice that of BLK, indicating that methylation is more important in HCRT. Similarly, Cd and As have substantially higher yields from HCRT than BLK. Given the similarity in atmospheric inputs, this suggests that HCRT has a lower retention of these elements than BLK, or has sources in the watershed besides atmospheric input.

A comparison of the stream export and throughfall input flux, taking into account the fact that about

50% of the moisture input to the watersheds is lost by evapo-transpiration (Castro and Morgan, 2000), illustrates that Hg and Pb are strongly retained in the watersheds, while As, Se, and Cd are more mobile, especially in HCRT (Table 7). For Cd, the retention in BLK is almost twice that of HCRT. As mentioned above, pH differences between these streams could account for the higher mobility of Cd in HCRT. The yields for Hg and MMHg are similar to those found for other streams in Maryland (Lawson *et al.*, 2000) while those for Cd and Pb are lower than those for larger watersheds in Maryland (e.g. Potomac and Susquehanna) and even for those that are relatively unimpacted (e.g. Rappahannock). Overall, the retention estimates are of similar magnitude to those made by others for similar forested streams (e.g. Church *et al.*, 1998).

The high retention of metals such as Hg and Pb in the watershed suggests that there has been a buildup of these metals in the last century due to anthropogenic inputs into the atmosphere and their subsequent deposition to remote locations. This has been demonstrated by measurement of soil Hg concentrations in various locations in the mid-west USA (Nater and Grigal, 1992). Thus, while emissions of these metals may be decreasing due to regulation there is still a large insult from the past stored in the watersheds. Thus, these metals will be slowly bled into the streams for years, for the more mobile elements, to decades for such elements as Hg and Pb. Thus, elevated stream concentrations of these elements will persist even after cessation or reduction in atmospheric inputs.

The results of the deposition and stream monitoring program show that, on average, the inputs to the two streams are similar and outputs, while comparable for total Hg, differ for the other elements. Detailed analysis of the data show differences on a smaller scale (e.g. seasonally) and there are strong differences in concentration between high and low flow periods in the streams. However, the similarity in inputs between these two watersheds confirm that any large difference in biota concentration between the two streams is presumably a reflection of differences in chemical composition and speciation in the stream waters, and differences in food chain structure and feeding behavior of organisms in the

Table 7. Watershed yields for each metal/metalloid for the two watersheds (BLK = Blacklick; HCRT = Herrington Creek tributary) and the estimated fraction of the throughfall input that is retained within the watershed

Parameter	BLK yield[a]	HCRT yield	BLK % retained[b]	HCRT % retained
Total Hg	17.7	14.7	85	86
MMHg	0.12	0.25	—	—
Cd	0.09	0.67	92	49
Pb	0.65	0.55	83	91
As	5.6	8.8	< 10	< 10
Se	1.7	1.6	71	66

[a] The yields are estimated based on the measured concentrations under the different flow regimes (base and high flow) and the actual flow data for the year of study. See text for details. Units are µmol m^{-2} yr^{-1} except for Hg and MMHg which are nmol^{-2} yr^{-1}.
[b] The percent retained is estimated as the percentage of the throughfall input (Table 2) that is found in the stream export in that year.

streams (Mason *et al.*, 2000a). The results from this study provide a unique dataset with which to examine the whole watershed process, from atmospheric deposition to release and transport of the metals and metalloids in the stream. Additionally, these results can for the first time be directly linked to the concentration of these elements in stream biota (Mason *et al.*, 2000a).

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